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## PREFACE

Four papers were presented at the Annual Meeting of the American Ceramic Society in New York City during the period April 31 - May 3, 1962. Their titles are as follows:

1. Properties of Several Boron Phosphate-Silica Devitrified Compositions.
2. Devitrified Pure Barium Titanate Dielectrics.
3. Structural Analysis of a Boron Phosphate-Silica Glass and Its Physical Properties.
4. Impact Strength of Glasses and Polycrystalline Ceramics.

A meeting was held with representatives of the Titanium Alloy Division (TAM) of National Lead Co., the Signal Corps and Rutgers University concerning ferroelectrics barium titanate in particular, in the form of sub-micron crystals and as a glass. The progress and techniques developed by the Signal Corps and by Rutgers University were reviewed. The TAM representatives expressed considerable interest in these types materials and have offered their services.

Mr. David A. Lupfer, a physicist, has recently been added to the staff of this research project on a half-time basis.

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Part I

DEVITRIFIED FERROELECTRICS

Abstract

Devitrified bodies were made and evaluated from the C.P. grade flame-sprayed barium titanate. The Curie temperature was shifted to higher temperatures, being as high as 155°C depending upon thermal history. Under certain conditions the dielectric constant retained its higher value above the Curie temperature. These results were compared to those of C.P. solid phase reacted barium titanate bodies and capacitor grade devitrified bodies.

The microstructures of the bodies were investigated. The devitrified barium titanate bodies result in the formation of extremely small crystals as compared to the large ones of the solid phase reacted barium titanate.

Part II

LOW LOSS BORON NITRIDE CERAMIC DIELECTRICS

Abstract

A method for testing electrical properties under humidity conditions was developed. By use of surface resistance measurements it is indicated that the problem is one of a surface nature. Also some boron nitride bodies were prepared conventionally.

Part III

STRUCTURAL STUDIES OF POLYCRYSTALLINE CERAMICS

Abstract

Metallization of micromodule substrates was found to be compatible with thermal conditioning treatment. The two processes can be combined within a single operation to result in greatly strengthened substrates.

Part IV

HOT EXTRUSION

Abstract

The capability of the hot extrusion equipment was demonstrated by the extrusion of a solid slug of aluminum metal and the coextrusion of aluminum clad, glass bonded mica. However, the quality of the coextrusions was not satisfactory. An experiment showing the flow pattern of the materials during extrusion is described.

Part V

LOW LOSS MICROWAVE CERAMIC DIELECTRICS

Abstract

Considerable difficulty has been encountered in the preparation of the lanthanum oxide-alumina-silica type composition. The evaluation of this material with a fritting procedure and an after-fire heat treatment has resulted in ceramic bodies of low maturing temperatures, longer firing range and low power factors.

- iii -

With the magnesia-zirconia titania system, low loss specimens have been prepared with a dielectric constant of approximately 19 at 1Mc.

Progress Report - Part I  
DEVITRIFIED FERROELECTRICS

Introduction

The most common ceramic ferroelectric barium titanate is characterized by a dielectric constant of approximately 1200 in the range from 0° to 110°C. A Curie point is reached at 120°C at which the dielectric constant rises very abruptly to 6000-8000, then decreases to some low value as the compound is no longer ferroelectric. An inversion from the tetragonal to the cubic phase takes place at this temperature.

Anliker, Brugger and Kanzig<sup>1</sup> studied fine particles of barium titanate powder by X-ray diffraction, electron diffraction and electron microscopy. They state that the transition from the tetragonal to the cubic phase of barium titanate becomes smeared out over a temperature range which increases with decreasing particle size.

If small crystals of barium titanate could be obtained in the bulk form of a ceramic body, the Curie temperature should increase. This is difficult to attain even with small crystals in the initial material since the crystals tend to grow rapidly during firing.

One approach is to start with a glass, and then by proper heat treatment, control the nucleation and growth of crystals. The making of a pure barium titanate glass has been

1. M. Anliker, H. R. Brugger, and W. Kanzig, "The Behavior of Colloidal Ferro-Electrics III, Barium Titanate BaTiO<sub>3</sub>" Helvetica Physica Acta., 27 (FASC 2) 99-124 (1954).

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accomplished by the flame spray technique. The barium titanate is melted at a high enough temperature, starting with fine particle sizes, and flame sprayed into a container of water, being cooled extremely rapidly. This procedure is thoroughly described in previous reports.

TAM capacitor grade and C.P. grade barium titanate have been investigated. The flame sprayed capacitor grade barium titanate contains some incipient crystallization while the flame sprayed C.P. grade is amorphous according to X-ray diffraction, petrographic, and DTA studies.

The objectives of this report are:

1. To fabricate specimens from the glass and to devitrify and mature these specimens during a second firing.
2. Evaluate the electrical and physical properties of the devitrified bodies.
3. Compare the devitrified bodies with sintered barium titanate bodies.
4. Examine the microstructures of the devitrified bodies.

#### Procedure

A small amount of water is added to the flame-sprayed material (-325 mesh) and pressed into discs which fire to 1/2 inch in diameter by 0.06 inches. The specimens were fabricated on a hand operated hydraulic press at 10,000 lbs. pressure.

The specimens were fired in a platinum wound furnace at a rate of  $7^{\circ}\text{C}/\text{minute}$ . The firing cycle was controlled by a Minneapolis-Honeywell Program Controller containing current proportioning control and a saturable core reactor.

The specimens reacted with all setter materials investigated including zirconia and platinum. A setter was made out of platinum such that the pressed specimen balanced on two small knife edges. Warping did not occur during firing. The small amount of platinum present from the knife edges was easily removed by a short grinding period using 600 grit silicon carbide paper and water.

The surfaces of each disc were coated with #5052 silver preparation manufactured by the DuPont Company and fired to  $760^{\circ}\text{C}$  in an electric furnace. A bath of Dow Corning 200 fluid containing a stirring rod and heating element was used to heat the specimens while taking electrical data. The electrical properties were evaluated at 1 Kc per second on a General Radio Company Impedance Bridge, Type 615A.

The microstructures were studied using the polished section technique. On a brass lap wheel with silicon carbide paper and water the specimens are ground with grain numbers 120, 240, 340 and 600. They are then ground in sequence with emery papers (0,2/0, 3/0, and 4/0) and kerosene, and polished with diamond and oil. The mounted specimens were etched with a solution of 1%  $\text{HNO}_3$  and 0.5%  $\text{HF}$ . Particle size distributions, phase estimations, and camera lucida tracings were made.

## Results and Discussions

### C.P. Grade Devitrified Bodies

The bulk densities of the C.P. grade devitrified  $\text{BaTiO}_3$  at  $1320^\circ\text{C}$  and  $1355^\circ\text{C}$  were respectively  $5.16\text{g/cc}$  and  $5.03\text{g/cc}$ .

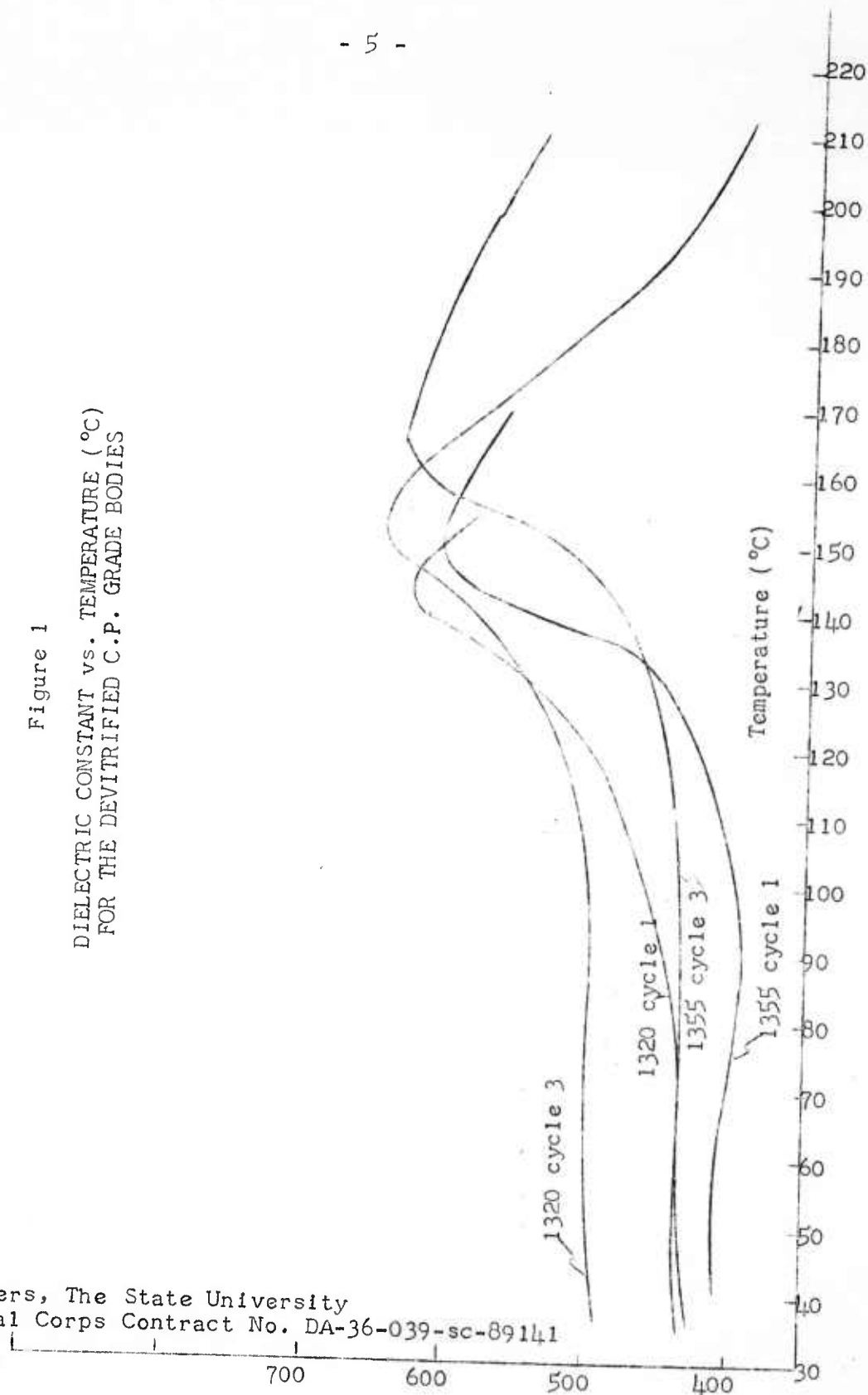
The dielectric constant versus temperature curves at one kc/second for the body at  $1320^\circ\text{C}$  and  $1355^\circ\text{C}$  are given in figure 1 on page 5. Their room temperature dielectric constants are between 400-500. The specimens were thermal cycled several times. The Curie temperatures as indicated by the peak in the dielectric constant-temperature curve for both bodies increased with thermal cycling. The Curie temperature for the body fired to  $1320^\circ\text{C}$  was increased from  $135^\circ\text{C}$  to  $141\text{-}143^\circ\text{C}$ ; that of the  $1355^\circ\text{C}$  body was increased from  $142^\circ\text{C}$  to  $155^\circ\text{C}$ . The Curie temperature dielectric constants are between 600 and 650. Above the Curie temperature the dielectric constant does not drop off as rapidly for the  $1355^\circ\text{C}$  body as does that for the  $1320^\circ\text{C}$  body. The  $1355^\circ\text{C}$  fired specimen sustains its higher dielectric constant through the maximum temperature, namely  $200^\circ\text{C}$ .

X-ray diffraction powder patterns of the devitrified  $1355^\circ\text{C}$  body were studied on a high temperature X-ray diffraction unit. The phase change from tetragonal to cubic occurred near the  $120^\circ\text{C}$  transition temperature, but over a  $20^\circ$  interval of  $15^\circ$  starting at  $110^\circ\text{C}$ .

To further observe this behavior, the appearance of hysteresis on a cathode ray oscillograph has been investigated. The solid phase reacted bodies show their familiar hysteresis

Figure 1  
DIELECTRIC CONSTANT vs. TEMPERATURE (°C)  
FOR THE DEVITRIFIED C.P. GRADE BODIES

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loops but at the present time however the devitrified bodies have shown no hysteresis. The low bulk densities of the devitrified specimens may be the reason.

The investigation of the unusual behavior of these bodies will continue.

A camera lucida drawing, figure 2 on page 7, emphasizes the detail of the microstructure of the 1355°C body. The particles or crystals (enclosed areas) are embedded in a matrix material. The hatched areas represent pores. The surface of the matrix material is more readily attacked by the etchant than are the surfaces of the crystals. The particle size distribution for the 1355°C body is given in figure 3, on page 8. This represents a volume distribution as determined statistically by the point count method. Five hundred (500) counts were made and are plotted as frequency against particle size. Most crystals fall in the range from the limits of resolution to 4 microns. The phase estimation is 48.8% crystal, 26.0% matrix material, and 25.2% pore and is given in Table I on page 9. From this it would appear that 90% of the crystal volume contains particles ranging from the limits of resolution (approximately 0.2 microns) up to 4 microns.

A petrographic study of the other firings will be reported next time.

#### Comparison of C.P. Solid Phase Reacted Body With C.P. Devitrified Body

The solid phase reacted C.P. body was fired in air at 1310°C for a two-hour soaking period, reaching a bulk density



Figure 2  
C.P. Devitrified 1355°C

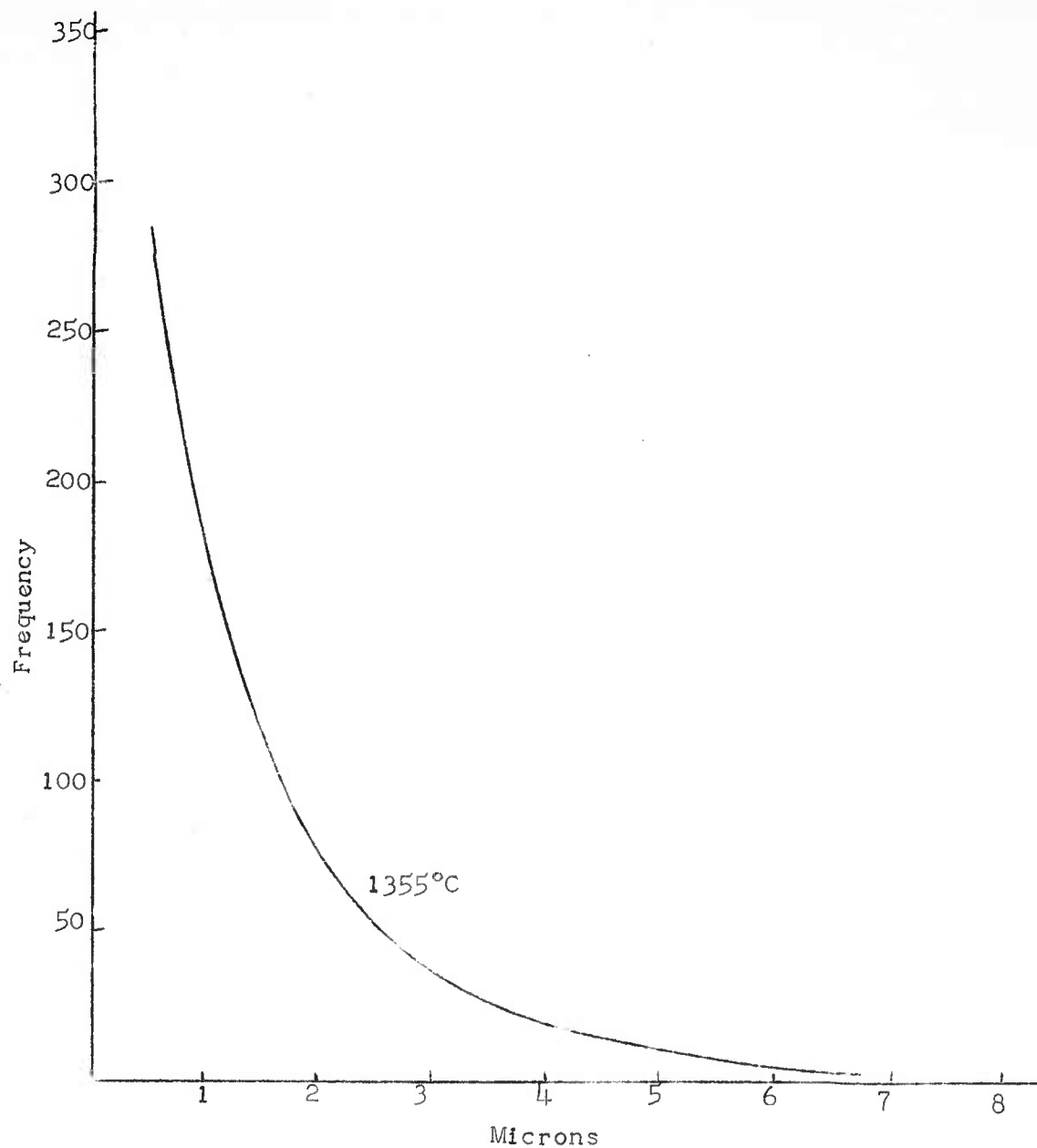


Figure 3

CRYSTAL SIZE DISTRIBUTION  
FOR C.P. DEVITRIFIED BaTiO<sub>3</sub>

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of 5.50g/cc. The dielectric constant versus temperature curve is plotted in figure 4 on page 10, for comparison with those of the devitrified bodies. The dielectric constant versus temperature curve is typical of sintering barium titanate. Detail of the microstructure is shown in the camera lucida tracing in figure 5 on page 11.

The crystal size distribution is given in Figure 6 on page 12. The crystals are considerably larger as compared to those of the devitrified bodies. In the devitrified bodies most crystals were in the size range from the limit of resolution to 4 microns. The grain size in the solid phase reacted body falls between 10 and 80 microns.

The pore to non-pore ratio was determined as 19.7% pore and 80.3% non-pore given in Table I on page 9. The crystal to glass ratio was not determined since it was difficult to use the point-count method, the only possible glass being crystal boundary material, which is very little.

Table I  
Phase Estimation

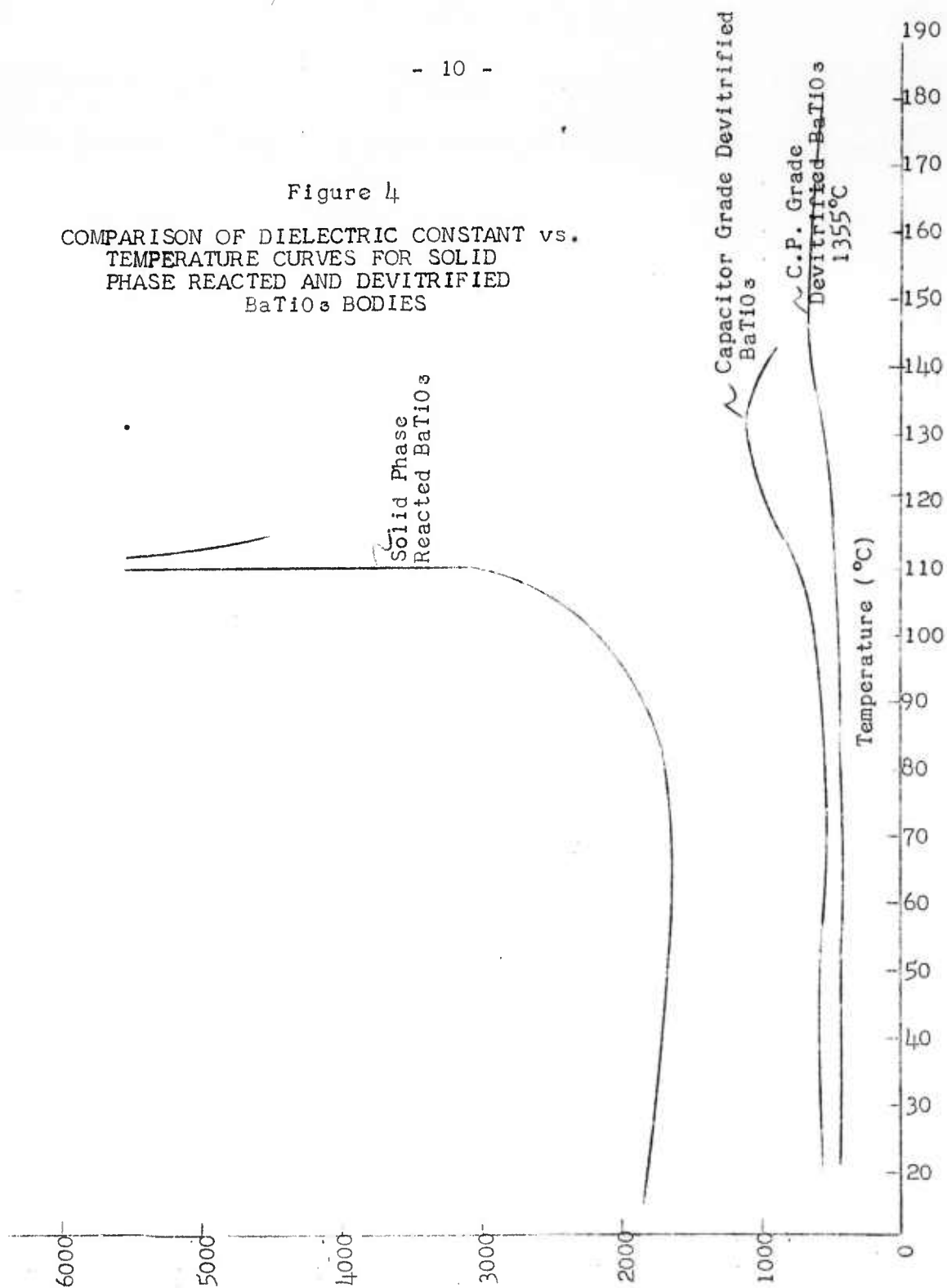
<u>Body</u>	<u>Void (%)</u>	<u>Crystal (%)</u>	<u>Matrix Material (%)</u>
C.P. Devitrified -1355°C	25.2	48.8	26.0
Cap. Devitrified -1360°C	31.4	51.6	17.0
C.P. Sintered -1310°C	19.7	80.3	----

Capacitor Grade Devitrified Barium Titanate

The devitrified body made of capacitor grade BaTiO<sub>3</sub> reached a maximum bulk density of 4.79g/cc at 1360°C. Its



Figure 4  
COMPARISON OF DIELECTRIC CONSTANT vs.  
TEMPERATURE CURVES FOR SOLID  
PHASE REACTED AND DEVITRIFIED  
BaTiO<sub>3</sub> BODIES



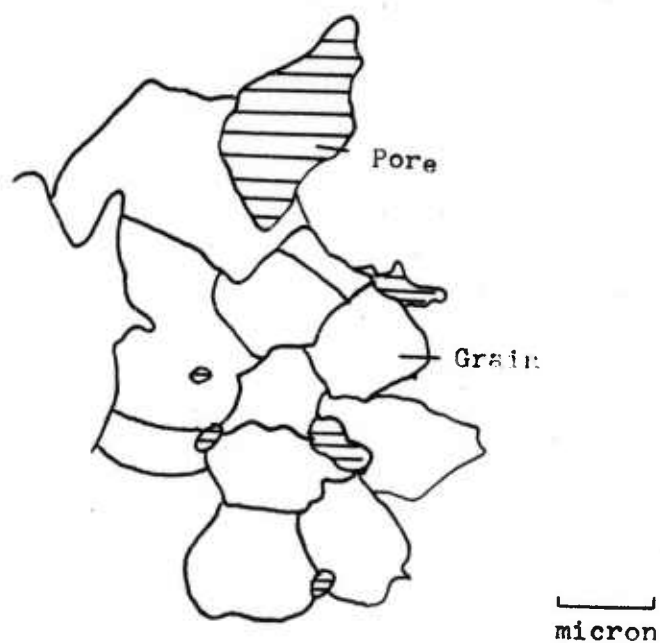


Figure 5  
Solid Phase Reacted 1310°C

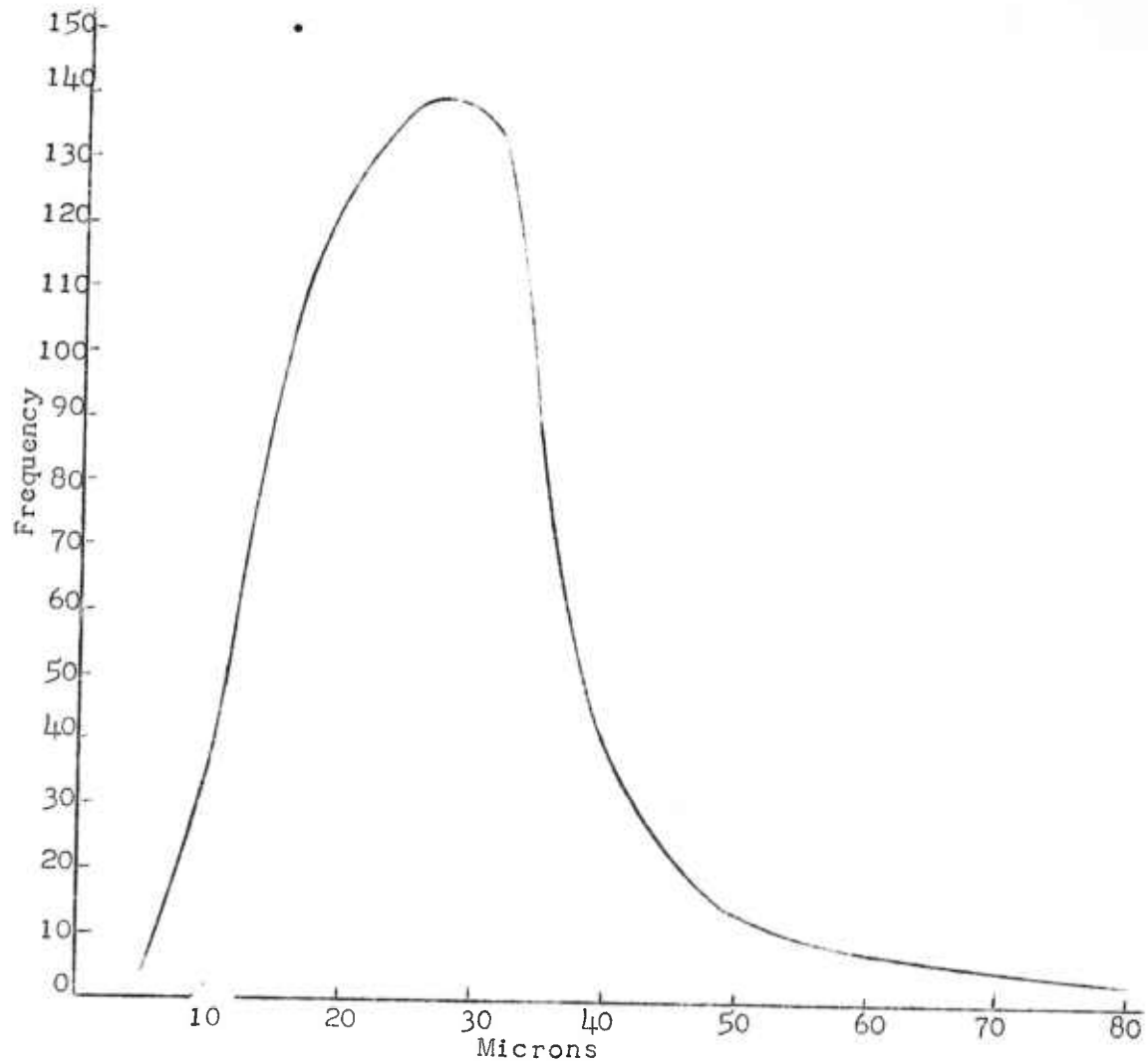


Figure 6

CRYSTAL SIZE DISTRIBUTION FOR  
C.P. SOLID PHASE REACTED  $\text{BaTiO}_3$

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Curie temperature was shifted to  $141^{\circ}\text{C}$  as shown in Figure 4 on page 10.

There are two ranges of particle size distribution for this body, which are given in Figure 7 on page 14. One is from the limit of resolution to 4 microns and the other from 4 to 12 microns. The latter is attributed to the incipient crystallization present in the capacitor grade flame-sprayed material while the former to nucleation and crystal growth from the glass present.

The particle size distribution of this body is very non-uniform as compared to those of the C.P. grade  $1355^{\circ}\text{C}$  and  $1320^{\circ}\text{C}$  devitrified bodies which are made from a more glassy material.

The phase estimation of the relative amounts of glass, crystal, and void is given in Table 1 on page 9 as 51.6% crystal, 17% glass, and 31.4% pores.

A comparison of the particle or crystal size distribution of the C.P. solid phase reacted material, C.P. devitrified and capacitor devitrified is shown in Figure 8 on page 15. The solid phase reacted material results in a large percentage of crystals in the 10-40 micron range as would be expected. In the case of the devitrified bodies, the crystals are much smaller with the C.P. grade exhibiting approximately 90% of the crystals finer than 4 microns. Obviously the devitrified process results in much finer crystal size in barium titanate.

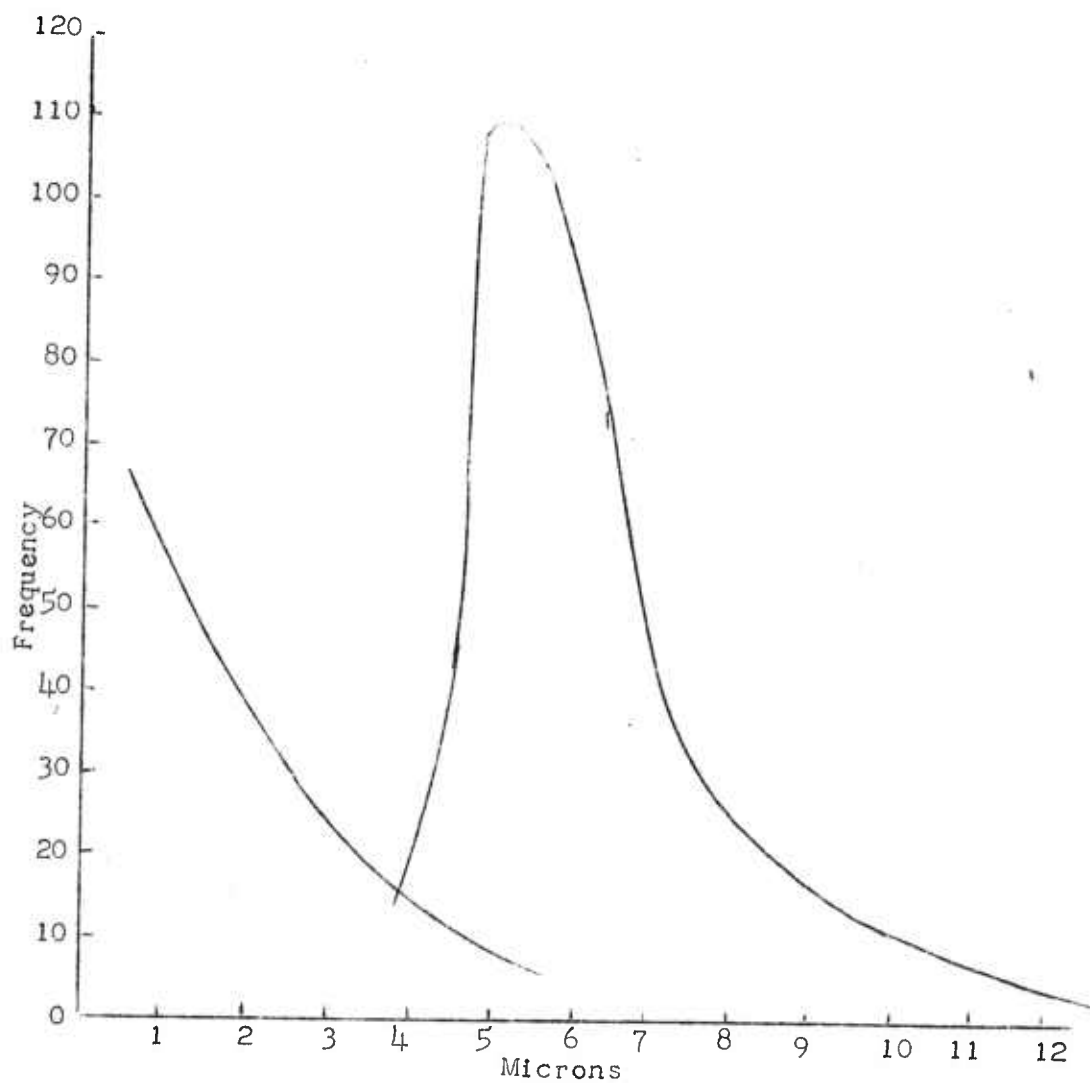
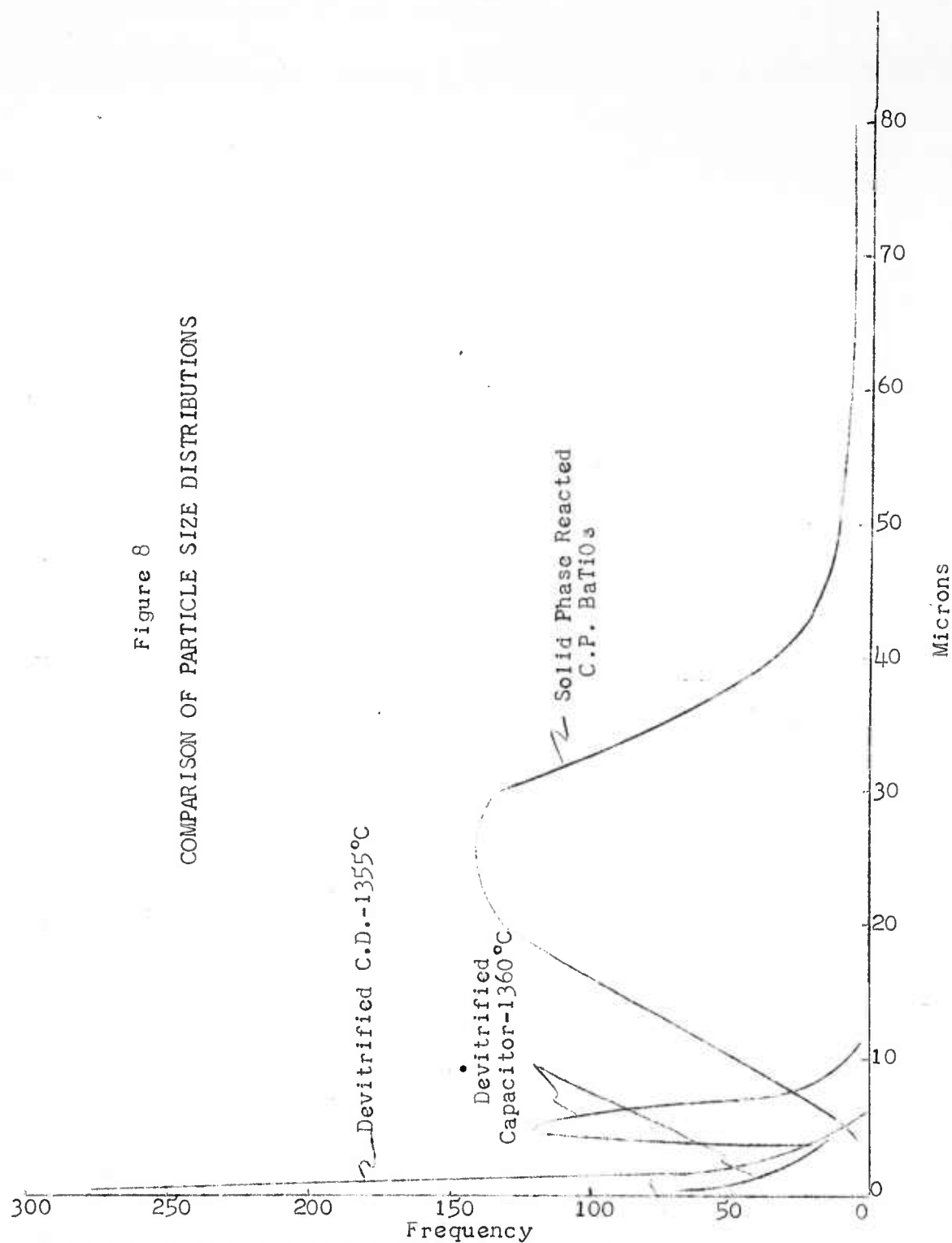


Figure 7

CRYSTAL SIZE DISTRIBUTION FOR  
CAPACITOR GRADE DEVITRIFIED BaTiO<sub>3</sub>

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Figure 8  
COMPARISON OF PARTICLE SIZE DISTRIBUTIONS



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### Summary

Devitrified bodies were made and evaluated from the C.P. grade flame-sprayed barium titanate. The Curie temperature was shifted to higher temperatures. This was as high as 155°C depending upon thermal history with the dielectric constant remaining higher above the Curie temperature than below under certain conditions. The crystal size distribution was found to be between the limits of resolution and 4 microns. This is extremely small as compared to the crystal size distribution of the solid phase reacted C.P. grade material, which was between 10 to 80 microns. The capacitor grade crystal size distribution is much less uniform than that of the C.P. grade devitrified barium titanate. Two-regions of crystal size distribution are shown: Limits of resolution of 4 microns and 4 to 12 microns. Thus the C.P. barium titanate glass is prepared into bodies and devitrified in a subsequent firing result in the formation of extensively small crystals resulting in an increased Curie temperature and a higher dielectric constant remaining above the Curie temperature as compared to below it.

### Future Work

1. Work is in progress to increase the bulk densities of the devitrified bodies.
2. The behavior of the dielectric properties versus temperature, especially in the Curie temperature region, will be further investigated.
3. The crystallization of the C.P. glassy material

will be further investigated in order to determine the optimum time-temperature conditions for the attainment of small crystals.



Progress Report - Part II  
LOW LOSS BORON NITRIDE CERAMIC DIELECTRICS

Introduction

Boron nitride, in solid and powder form, has a hexagonal crystalline structure similar to graphite. The solid form is a dense, strong, self-bonded body whose properties are directional because of the partial orientations of the plate-like crystals during fabrication. The most interesting property is the excellent electrical properties including high resistivity, low loss and high dielectric strength, even at elevated temperatures.

At low and moderate temperatures its resistivity approximates that of high alumina ceramics. Under conditions of very high relative humidity, its resistivity is somewhat lower. Its dielectric strength is in excess of 250 volts per mil. At high frequencies, the dielectric constant of boron nitride does not vary in the temperature range between 75° and 900°F. Tables I and II show the electrical properties as reported by the Carborundum Company.

Table I

ELECTRICAL PROPERTIES

Frequency c/s	Dissipation Factor		Dielectric Constant			
	75°F	600°F	900°F	75°F	660°F	900°F
A Direction						
10 <sup>2</sup>	0.00103	0.032	1.0	4.15	4.4	9.0
10 <sup>4</sup>	0.00042	0.0043	0.1	4.15	---	4.5
10 <sup>6</sup>	0.00020	0.0012	0.0056	4.15	---	4.25
10 <sup>8</sup>	0.000095	-----	-----	4.15	---	4.15
B Direction						
10 <sup>10</sup>	0.0003	0.0004	0.0005	4.80	---	4.80

A Direction - Measured parallel to molding pressure  
 B Direction - Measured perpendicular to molding pressure

Table II

RESISTIVITY vs. HUMIDITY

R. H. %	Resistivity at R.T. (ohm-inches)
20	3.9x10 <sup>11</sup>
50	2.9x10 <sup>10</sup>
90	1.9x10 <sup>9</sup>

The above table will be used as a reference later in this report and the reports that follow.

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It is obvious that the electrical properties are excellent and are in the ultra low loss range, however, they are markedly effected by moisture. The Signal Corps have noted that electrical properties deteriorate quite readily under high humidity conditions. This limits the use of boron nitride as high frequency insulation. The overall objectives of this work is to attempt to find a way of minimizing or eliminating this effect of humidity on electrical properties, while retaining these excellent properties.

This report deals with two approaches to the overall problem. They are 1) to develop a method of determining and evaluating the effect of humidity on the electrical properties of boron nitride and 2) to develop bodies retaining the desirable properties of boron nitride yet eliminating the effect of humidity.

#### Procedure

##### A. Specimens Prepared from Powdered Boron Nitride

Various attempts were made to prepare a BN body by conventional methods. The raw materials for this phase was obtained from the Carborundum Company in the form of acid washed trimmings from their hot pressed materials. Its composition is listed below.

Table IV

<u>Composition</u>	<u>Wt%</u>
BN	99.50
B <sub>2</sub> O <sub>3</sub>	0.05
Alkaline earth oxides	0.10
Al <sub>2</sub> O <sub>3</sub> and SiO <sub>2</sub>	0.21
C	0.05

The powder was dry pressed into various sized pieces and fired to various temperatures to determine the best maturing temperature. It was found that bodies fired between 2150°F and 2350°F had the best properties. Also some sample were fired in a nitrogen atmosphere but these didn't mature at temperature as high as 2800°F.

B. Electrical Testing at Various Humidities  
(Power Factor and Dielectric Constant)

The procedure consists of connecting heavy leads from a standard Q meter (Boonton 260-A) to a sample in a sealed jar. The jar is 3 1/2 inches in diameter by 6 3/4 inches high. They are sealed by means of a screw cap. The sample holder consists of two pieces of metal clamped to the leads which extended through the top of the jar. These leads are then connected to the Q meter by use of heavy steel wires. The set up is shown in Figure 1 page 22.

To attain the necessary range of humidities in the jars a solution of glycerol and water in various proportions is used as listed below.

Table III  
Glycerol-Water Mixture  
Relative Humidity at 25°C

<u>Wt% Glycerol</u>	<u>Relative Humidity %</u>
0	100
15.5	97.1
25	92.7
35	85.2
50	73.3
60	62.3
75	44.3
83	33.8
92	16.9
98	1.7

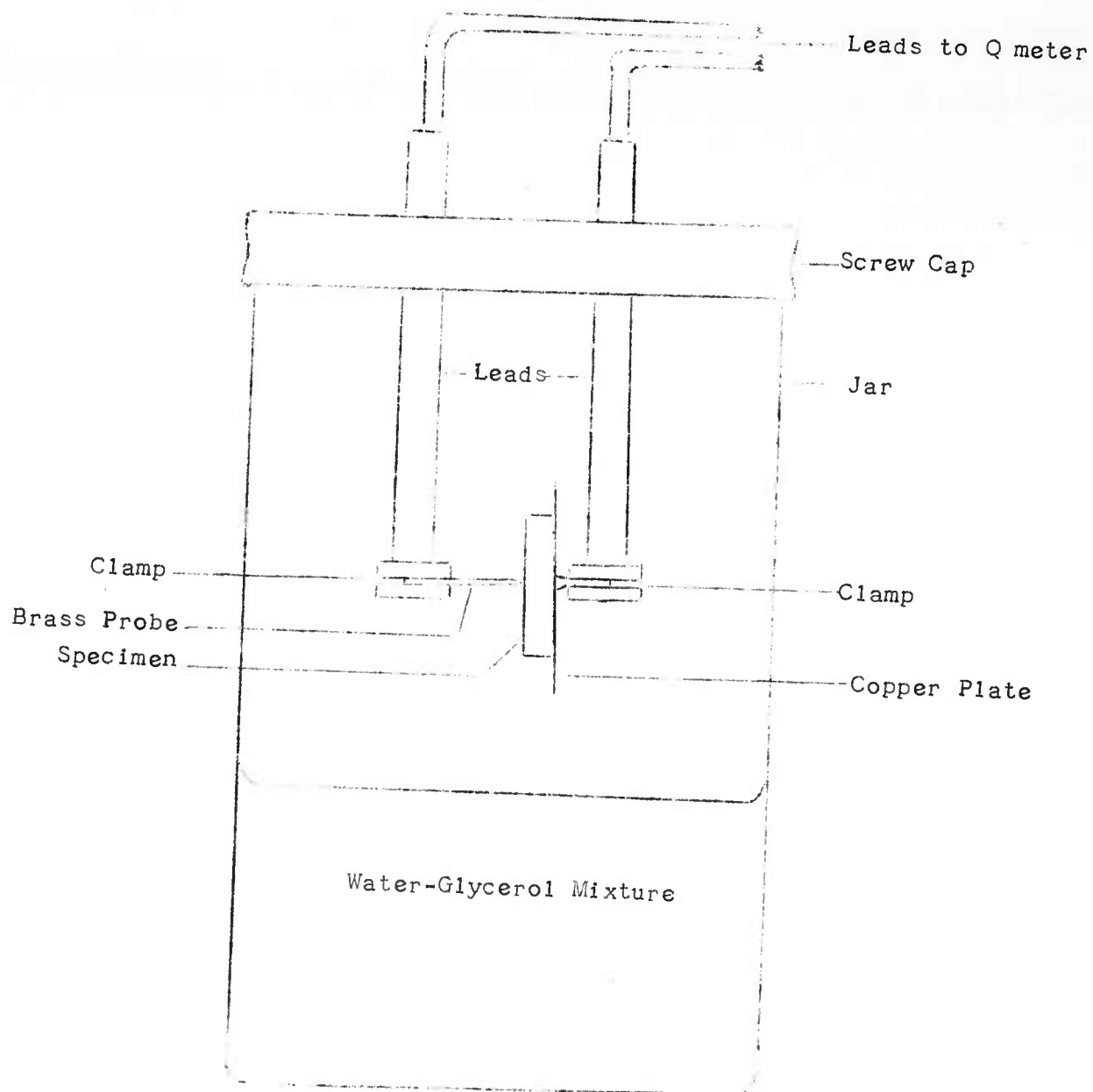


Figure 1

The solutions reach equilibrium in approximately 1 hour in the sealed jar and all measurements are made after their period of time. There are two sets of measurements necessary to obtain the power factor and the dielectric constant. They are the measurements of the C and Q for the sample holder and these C and Q for the sample in the sample holder. The power factor (P.F.) and dielectric constant (K) are determined in the following way.

1. Sample Holder Parameters:

a. Perform the standard Q meter tests with only the sample holder connected to the Q meter.

b. Find  $C_H$  and  $G_H$  as follows:

$$C_H = (\Delta C) = (C_1 - C_2) \quad \frac{G_H}{\omega} = \frac{C_1 (\Delta Q)}{Q_1 Q_2}$$

$C_H$  = Capacitance of holder  $G_H$  = Conductance of holder.

2. Sample in Sample Holder:

a. Perform the standard Q meter tests with the sample in the sample holder.

b. Find  $C_t$  and  $G_t$  as follows:

$$C_t = (\Delta C) = (C_1 - C_2) \quad \frac{G_t}{\omega} = \frac{C_1 \Delta Q}{Q_1 Q_2}$$

$C_t$  - Capacitance of sample and holder

$\frac{G_t}{\omega}$  - Conductance of sample and holder

3. Find K and P.F. as follows:

$$K = \frac{(C_t - C_H) t}{(.1766) d^2} \quad P.F. = \frac{(\frac{G_t}{\omega} - \frac{G_H}{\omega})}{(C_t - C_H)}$$

It was decided that in order to find an answer to the overall problem a better understanding of the material as produced industrially was necessary as this information was

not available. For this reason electrical measurements were taken on an industrial sample by the method stated above.

### C. Surface Resistivity Measurements

The surface resistivity tests were taken in order to determine whether this effect of humidity was due to surface effects only. The surface resistivity of the industrial material and those prepared from powdered B.N. were measured with a wheatstone bridge capable of measuring resistance up to  $10^{12}$  ohms. The specimens were placed in the jars described in (B) above with a slight modification in the sample holder.

### Results

#### A. Preparation of J- Series Samples

As stated above many bodics were prepared by conventional methods, but most of the specimens crumbled when handled and all dissolved in water. These samples were not as dense or as hard as the industrial hot pressed specimens. Sample J-5 of the prepared powdered boron nitride exhibited the best properties of all the samples prepared but was not as stable as the hot pressed industrial. The density of J-5 was determined very crudly by the weight of the sample and then determining its volume. Absortion test couldn't be preford because the sample would dissolve in water. The density was found to be  $1.95 \frac{\text{gm}}{\text{cm}^3}$  as compared to  $2.10 \frac{\text{gm}}{\text{cm}^3}$  of hot pressed sample.

#### B. Power Factor and Dielectric Constant

In this phase the P.F. and K of the industrial sample

were measured under various humidity conditions as described above. The purpose of this was to obtain a curve to use as a reference. Specimen J-5 of the prepared powdered boron nitride was measured under the same conditions to determine whether specimens of equal quality to the hot pressed material could be attained. It was felt that in order to solve the problem it would first be necessary to determine the quality that could be attained from powdered boron nitride. In Table V the electrical properties of both types materials are presented. The data is plotted in Figure 2 and 3 on pages 26 and 27. This data was taken after the specimens were allowed to remain for one hour in the humidity jars, this time being necessary for humidity equilibrium.

Table V

Humidity	Industrial Hot Pressed BN		Sintered BN (Sample J-5)	
	<u>P.F.(%)</u>	<u>K</u>	<u>P.F.(%)</u>	<u>K</u>
100%	-----not measurable-----			
93%	42.00	3.1	63.0	7.6
85%	21.00	6.3	27.5	6.2
73%	9.75	6.8	12.5	5.5
67%	1.90	7.8	2.5	4.1
44%	.21	4.6	.32	3.95
34%	.15	---	.20	----
Dry	.09	5.15	.105	5.15

The large difference in the power factor at 93% R.H. between the hot pressed and sintered samples is probably due to greater voids in the sintered peice. These greater



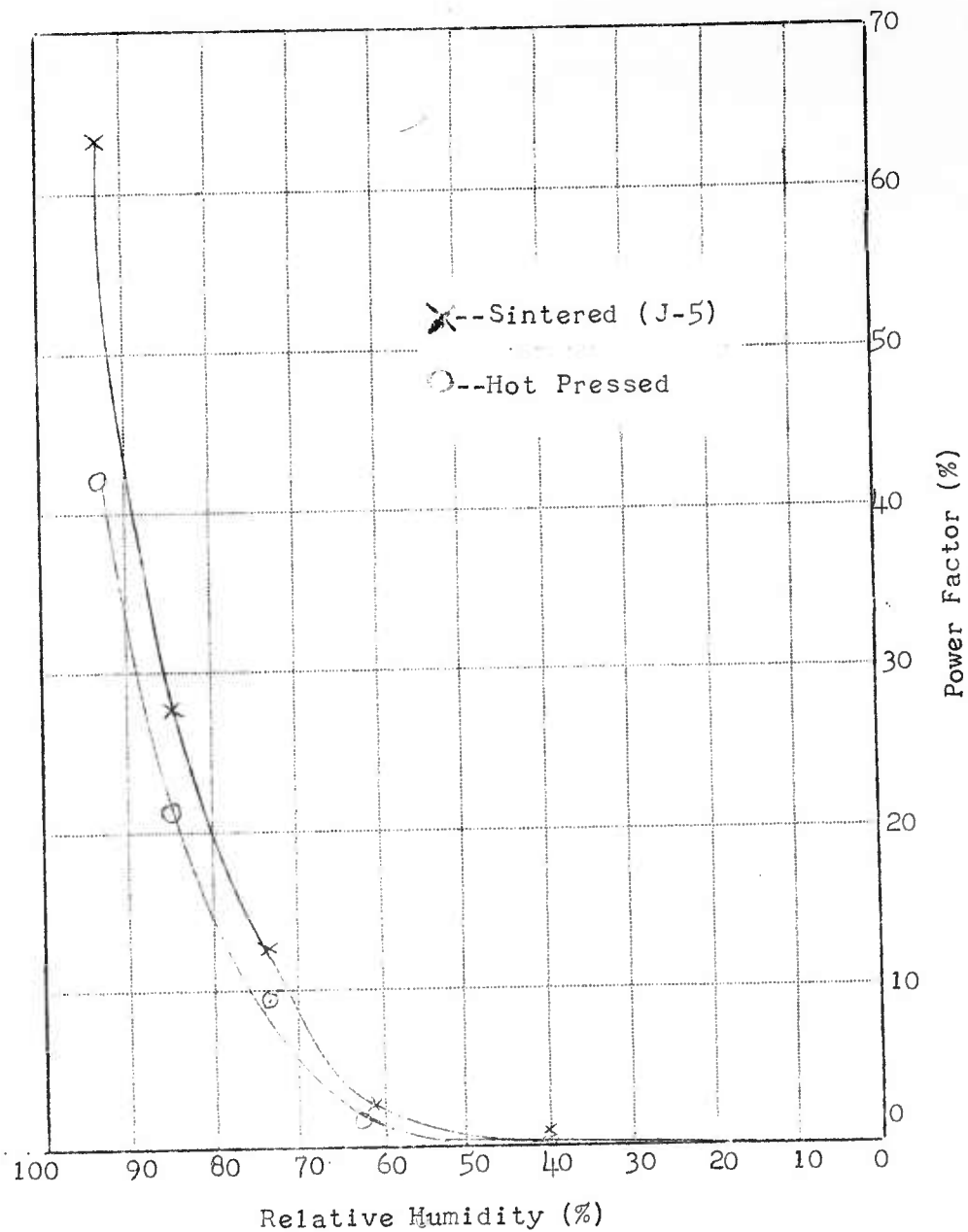


Figure 2

POWER FACTOR vs. RELATIVE HUMIDITY  
AT ROOM TEMPERATURE

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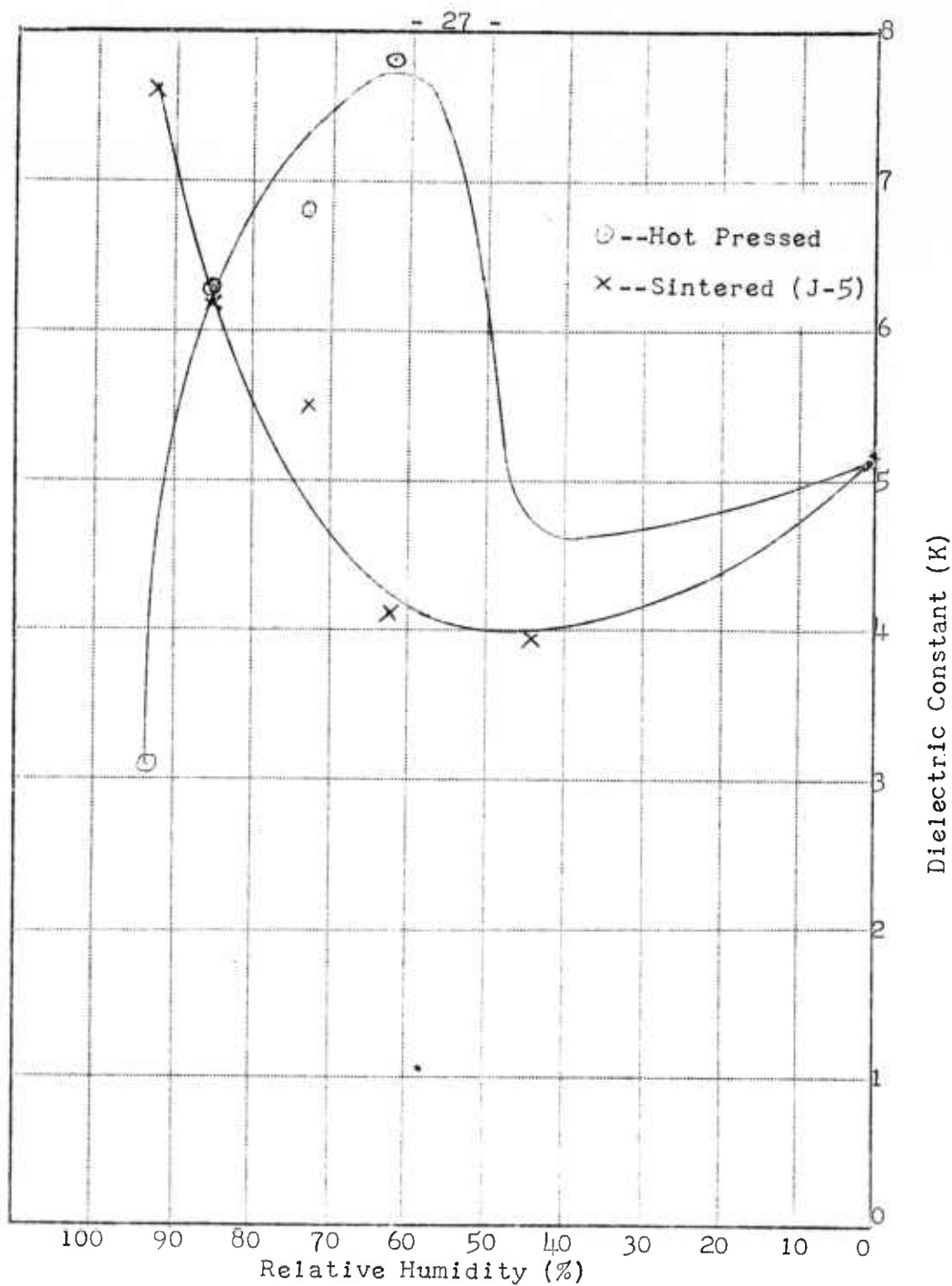


Figure 3

DIELECTRIC CONSTANTS vs. RELATIVE HUMIDITY  
AT ROOM TEMPERATURE

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void space is varified by the lower density aquired with the sintered sample.

### C. Surface Resistivity Properties

Surface resistivity measurements were taken in an attempt to determine the mode or reason for the deterioration of electrical properties in a humid atmosphere. It was reasoned that it should be due to a surface phemoncmon, as can be seen in Figure 4 on page 29, there is a definite change in surface resistivity at 100% relative humidity in both the hot pressed sample and in the J-5 specimen. Also it can be seen that the hot pressed sample levels off after approximately one hour (time required to reach equilibrium in P.F. measurements). At relative humidities of 75% and 50% if there is any differance, the value of surface resistivity after an hour is higher than  $10^{12}$  ohms. The larger difference in curves from 5 minutes to 60 minutes is attributed to the low density thus open pore volume of the sintered specimen. Thus in the case of the hot pressed specimen the resistivity reached the same value but only after one hour exposure. However, the fact that the resistivity is the same for both types of material after the hour exposure indicates that the surface of the hot pressed specimen has been effected and possibly to the same degree as the sintered specimen after 10 minutes.

### Summary

From the work thus far it has been indicated that the problem of the deterioration of the electrical properties

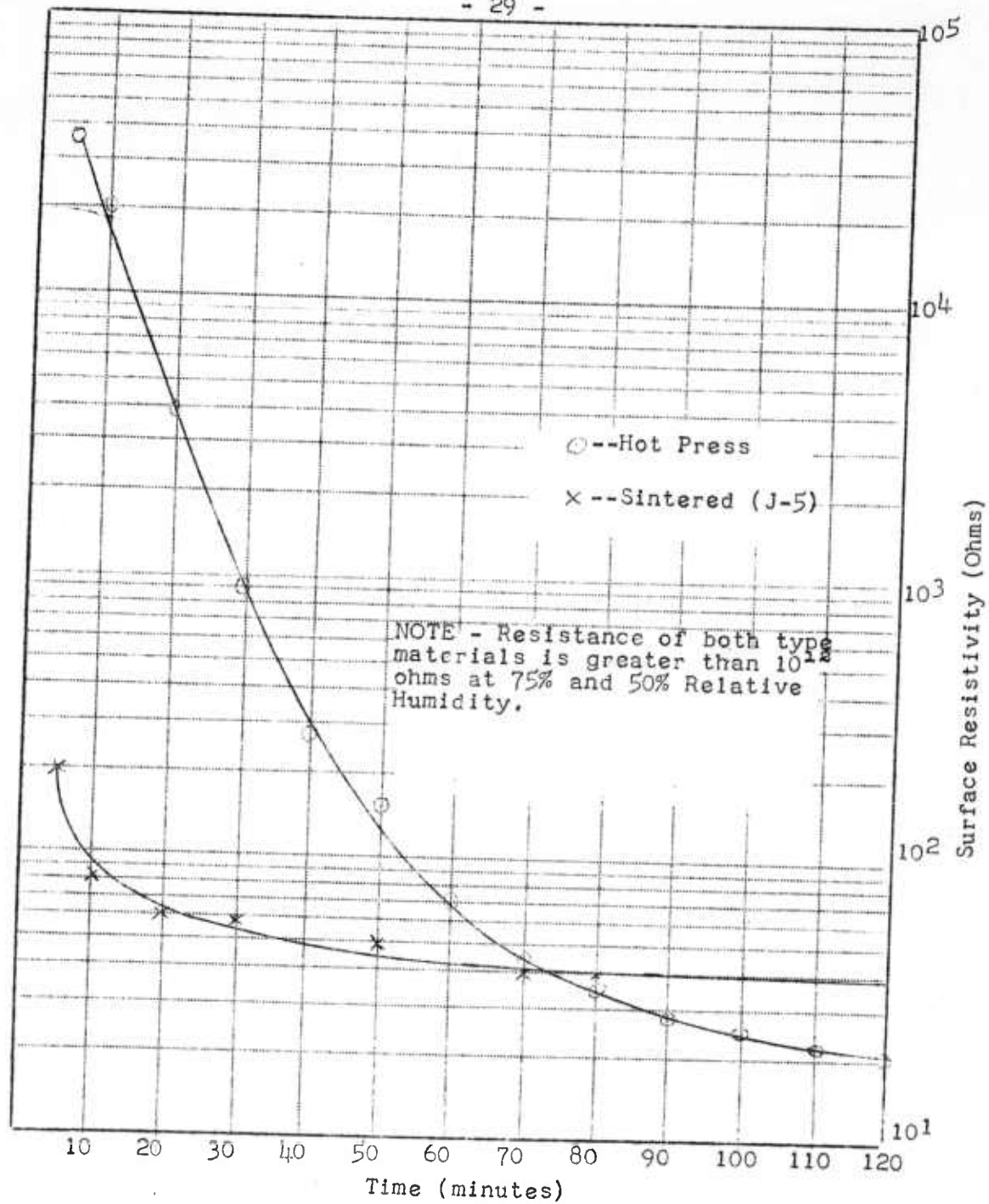


Figure 4

SURFACE RESISTANCE vs. TIME AT 100% R. H.

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of boron nitride in a humid atmosphere is a surface phenomenon. This is illustrated by the more rapid decreases in resistivity of the porous sintered specimen as compared to the impervious hot pressed specimen along with the equalization of this property for both materials after one hour exposure to 100% relative humidity. It is further indicated by the poor power factor of the sintered specimen at all humidities down to rather low humidities.

The electrical properties of hot pressed boron nitride are appreciably effected by humidity as low as 30% relative humidity.

#### Future Work

1. Continue study to learn mechanisms of electrical deterioration under high humidity conditions.
2. Continue study of glass-boron nitride type bodies
  - a. Investigate wettable glasses
  - b. Investigate sintering type firing
  - c. Investigate hot pressing.

Progress Report - Part III

STRUCTURAL STUDIES OF POLYCRYSTALLINE CERAMICS  
Factors Effecting Mechanical Strength  
of Ceramic Materials

Introduction

. This report is the sixth of a series dealing with the mechanical strength of ceramic materials fabricated as micromodules. The work here reported shows, at least for the American Lava Al 614 wafers, that metallization is not incompatible with thermal conditioning. Indeed, it was found that the two processes could be combined within a single operation.

Discussion

The process of thermal conditioning as applied to micro-modules has been discussed in reports one through five of this series. Alumina wafers have been strengthened more than 60% and the strength of a titania body has been more than doubled. Dimensions, camber, and electrical properties remained well within tolerance limits for all bodies tested.

As components of complete electronic devices, substrates must be metallized in a pattern appropriate to their function. The metallizing composition and the method of application are determined not only by wafer composition but by other factors as well. In all cases the metallizing must be fired on and matured over an extended period of time. If

the firing temperature is greater than that at which thermal conditioning has been carried out, it is to be expected that the effects of conditioning will be reduced or nullified. For this reason it was important to observe the effects of thermal conditioning when added as the terminal phase of the metallizing procedure.

Accordingly, 20 AL AL614 (94-96%  $Al_2O_3$ ) wafers were metallized with compound 80-20 Pt-Pd requiring a firing temperature of 2550°F. At completion of the 45 minute maturing period, the wafers were removed from the furnace and quenched in a stream of cool air for 1 minute at a distance of 5 inches from the blower orifice. Table I is a summary of strength test results.

Table I

	<u>As rec'd</u>	<u>Thermal Conditioning after metallization</u>	<u>Thermal Conditioning at 2500°F -no metallization</u>
MOR	34,000 psi	47,100 psi	55,400 psi
Max.	47,100	63,300	71,300
Min.	16,000	24,300	35,300
Range	31,100	39,000	36,000
Sample size	25	20	10
# within 10%	7	4	3
# within 20%	19	10	8
% greater than as rec'd MOR	---	39%	63%

These results are most encouraging. Examination of the sample statistics and the thermal conditioning curve led us to the conclusion that the temperature of the wafers at start of quench was approximately 2375°F. This means that during removal from furnace the temperature drop was

some 175°F. A reduction of temperature drop to 50°F would permit conditioning at the optimum temperature of 2500°F at start of quench. Thus there is no reason why these wafers, after metallization, cannot be increased in strength by the expected 60%.

Conclusion

R.C.A., Somerville Division, has suggested that a seminar be conducted to instruct industry in this application of thermal conditioning. If substrate vendors show sufficient interest, a seminar will be scheduled for the earliest possible date.



Progress Report - Part IV

HOT EXTRUSION

Introduction

The primary objective of this study is to produce barium titanate by hot extrusion which will be comparable or superior in quality to that which has been produced by hot pressing.<sup>1</sup> An extrusion process is considered to be more desirable than hot-pressing for production purposes. Although the primary effort in this work is to be directed toward the extrusion of barium titanate, the information obtained in this study should be applicable to the hot extrusion of numerous other ceramic materials.

The original extrusion attempts in this study were performed at Extrusions Inc., in Caldwell, New Jersey and were described in an earlier report.<sup>2</sup> This work was sufficiently successful to institute a program at Rutgers for the purpose of pursuing the investigation further.

1. A. Brown and R. Fisher, "Properties of Hot-Pressed Barium Titanate", USARDL Technical Report 2196, April 1961, U.S. Army Signal Research and Development Laboratory, Ft. Monmouth, New Jersey.
2. "Development of Ceramic Dielectrics", Progress Report No. V, Contract No. DA-36-039-sc-78084, September 1 to December 1, 1959, School of Ceramics, Rutgers, The State University, New Brunswick, New Jersey.

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The equipment and procedures used in the present investigation were described in the previous progress report.<sup>3</sup> In that report, three attempts to extrude a glass bonded mica composition in 1018 carbon steel cans were described. Successful extrusion was not obtained. Glass bonded mica was chosen for this work as it is known to be extrudable at fairly low temperatures. Since the equipment being used had not been tested previously it was felt that the use of a material of known extrusion characteristics would be helpful in this preliminary work.

#### Experimental Work and Results

Since, attempts to coextrude the glass bonded mica composition in 1018 carbon steel was not successful, it was decided to investigate a metal capable of being extruded more readily. This was deemed necessary to demonstrate whether or not the present equipment design was capable of successful extrusion under the proper conditions. The metal chosen for this work was aluminum since it is commercially extruded at temperatures from 650° to 950°F and the glass bonded mica should extrude at approximately 1000°F. The grade of aluminum recommended for extrusion by Alcoa was grade 1100F.

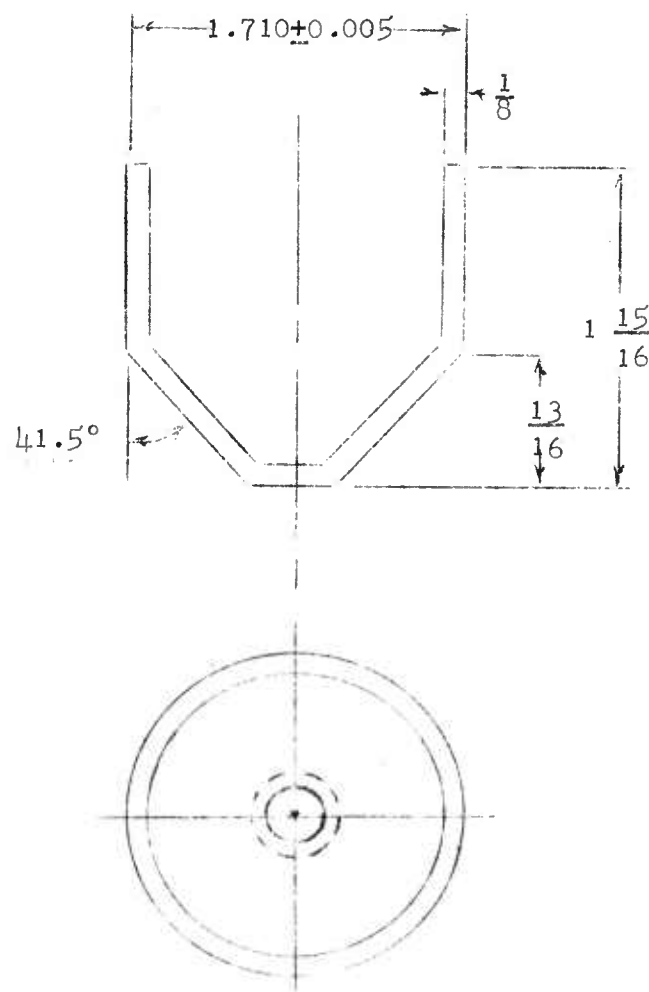
3. "Inorganic Dielectrics Research", Progress Report No. 1, Contract No. DA-36-039-sc-89141, November 1, 1961 to February 1, 1962, School of Ceramics, Rutgers, The State University, New Brunswick, New Jersey.

The first experiment in this series was performed using a solid aluminum billet rather than an aluminum coextrusion can. This was done to demonstrate whether the equipment was capable of extruding the aluminum itself. Thus, if the aluminum could be extruded by itself but not as a coextrusion can with the glass bonded mica, it would indicate that it was the ceramic and not the metal which was defeating the extrusion.

Extrusion of the solid aluminum billet was accomplished at room temperature and a gauge reading of approximately 108,000psi. The die and extrusion barrel were lubricated with a mixture of stearic acid and graphite. This extrusion was apparently of good quality having a uniform diameter and a smooth surface.

Next a series of extrusion experiments were performed with glass bonded mica in aluminum coextrusion cans. The design of these cans is shown in Figure 1 on page 37 and pertinent data for all extrusions are given in Table I. The first extrusion (Run #5) was performed at room temperature with the glass bonded mica powder having been hand-tamped into the aluminum can prior to extrusion. At the maximum gauge reading of 125,000psi only about a 1" long extrusion occurred. However, the aluminum coextrusion can had undergone considerable flow within the extrusion barrel since the side walls of the can were approximately twice as thick as they had been originally. It was felt

Figure 1  
ALUMINUM COEXTRUSION CAN



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Table I  
COMPLILATION OF HOT EXTRUSION DATA

Extrusion Run #	<u>Materials</u>		<u>Preheat Temperature (°F)</u>		Gauge Reading At Extrusion (psi)	Remarks
	<u>Coextrusion Can</u>	<u>Core Material</u>	<u>Coextrusion Can</u>	<u>Core Material</u>		
4	Solid Aluminum	billet <sup>1</sup>	Room Temperature		108,000	Smooth, uniform diameter extrusion. Only extruded about 1" length.
5	Aluminum	Glass Bonded Mica	Room	Room	125,000	Obtained co-extrusion but metal cladding ruptured and wall thickness very irregular
6	Aluminum	Glass Bonded Mica	1100	1100	83,000	Essentially the same as Run #6.
7	Aluminum	Glass Bonded Mica	900	900	83,000	Essentially the same as Run #6.
8	Aluminum	Glass Bonded Mica	Room	1100	83,000	Extrusion results were very similar to Run #6.
92	Aluminum	Glass Bonded Mica	900	900	83,000	Marker layer movement showed that central portion of core material exhibited large amounts of flow

<sup>1</sup>All aluminum used was type 1100F

<sup>2</sup>This run contained marker layers for observing flow patterns

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that hand-tamping of the mix into the coextrusion can did not result in effective compaction. As a result, the inward movement of the sidewalls of the coextrusion can was relatively unopposed during the initial stage of application of extrusion pressure. This observation led to devising a set-up for pressing the ceramic material in the coextrusion can at higher pressures. Since the cans were made of aluminum, they had to be supported to keep them from distorting under compacting pressure.

The next extrusion (Run #6) was performed with an aluminum coextrusion can into which the glass bonded mica mix had been compacted at 10,000 psi. The can containing the material was heated to 1100°F with a 1/2 hour soak and then transferred to the extruder barrel. Upon application of pressure a rather sharp report was heard and extrusion occurred at a gauge reading of approximately 83,000 psi. Coextrusion did occur and a length of about 9" was extruded. However, the extrusion was not of good quality. The aluminum cladding was ruptured in a number of places and the wall thickness of the aluminum cladding was very irregular. The report which was heard was believed to have been caused by the leading end of the extruded column blowing off. This was surmised to be a result of the glass bonded mica tending to extrude more readily than the aluminum and to low tensile strength of the aluminum. After the leading end of the extrusion blew off, the glass bonded mica apparently extruded through the aluminum pipe formed by the extrusion since a

considerable amount of glass bonded mica spaghetti was obtained. This spaghetti was remarkably round and uniform in diameter. After extrusion, the slug remaining in the extrusion barrel and some of the extruded material were cross-sectioned. The following parts are shown in Figure 2: a cross-section of the slug left in the extrusion barrel; cross-sections, both parallel and perpendicular to the extrusion direction, of a coextruded portion; an exterior view of a length of the extruded portion; and a piece of the glass bonded mica spaghetti.

The next extrusion attempt (Run #7) was performed under the same conditions as Run #6 except the aluminum can containing the glass bonded mica was only heated to 900°F. The results of this extrusion were almost identical to that of Run #6 except the glass bonded mica was apparently under-fired and the spaghetti was of poor quality.

Since lower extrusion temperature did not seem to enhance the extrusion, it was decided to heat the glass bonded mica but not the aluminum coextrusion can as the tensile strength of the aluminum would be higher at low temperature. A slug of glass bonded mica was cold-pressed and machined to fit inside the aluminum can. The glass bonded mica was heated to 1100°F with a half-hour soak and placed in the extrusion assembly. This extrusion (Run #8) was very similar to Run #6.

In order to study the flow pattern of the materials, a specimen was prepared in which a small amount of a coloring

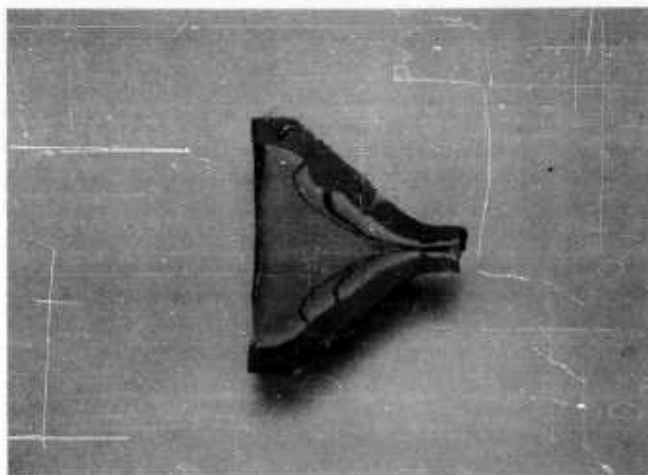


FIGURE 4  
Cross-section of Coextrusion  
Can After Extrusion Run #9

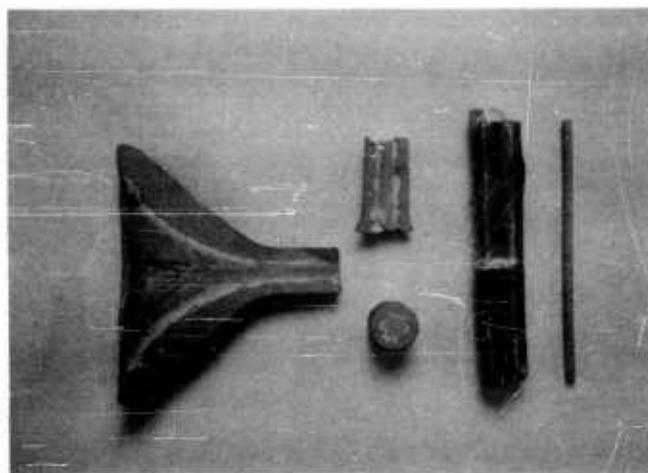


FIGURE 2  
Pieces Obtained From  
Extrusion Run #6

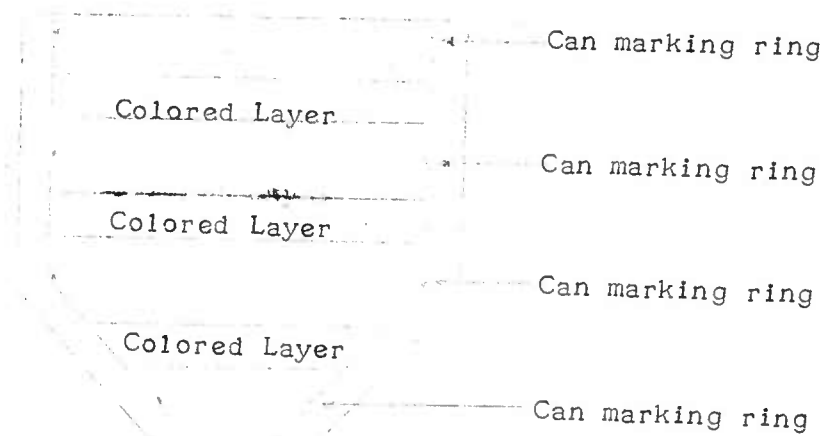


oxide was mixed with a small quantity of the glass bonded mica and thin layers of the colored material were added during the cold-pressing of the slug. Colored rings were also painted on the interior of the aluminum can. The markings were located approximately as shown in Figure 3. After extrusion, the markings on the can itself were rather indistinct and hard to analyze. However, the colored layers within the glass bonded mica were very clear. This assembly was heated to 900°F before extruding. A picture of a cross-section of the slug remaining in the extrusion barrel after extrusion is shown in Figure 4. The layer nearest the die was entirely extruded. The remaining two layers show that the central portion of the material exhibited by far the greatest amount of flow. It is also indicated that the material immediately adjacent to the can underwent somewhat more movement than the material a small distance in from the can. The large flow of the center portion probably occurred or at least was enhanced as a result of the glass bonded mica rupturing through the aluminum cladding. Studies of flow patterns may prove to be of considerable value in evaluating the effects of die or extrusion can design changes in future work.

#### Summary

Coextrusion of ceramic cores with metal cladding was accomplished. However, the quality of the extrusions were poor with the cladding thickness being very irregular. With

Figure 3  
LOCATION OF MARKERS IN COEXTRUSION CAN



the thin-walled ( $1/8$ " ) cans used in this work, it is apparent that there is a considerable tendency for these walls to flow inward during extrusion. It was also apparent that the greatest volume of material that extruded came from what was originally the central portion of the extrusion blank. It appears that the use of thicker walled coextrusion cans is desirable. It is believed that this will be advantageous in two ways. First, it may help to prevent the movement of the walls of the can in toward the center. Second, it may more nearly balance the relative volumes of ceramic and metal being extruded. If every portion of the original extrusion blank moved at the same rate during extrusion, it would be relatively simple to calculate the coextrusion can dimensions needed for a given cladding thickness. However, with the central portion of the ceramic material moving more than the outer portions (this is not unusual in normal, room temperature ceramic extrusions), a thicker walled can may be necessary in order to get the proper amount of metal to extrude as cladding.

A metal cladding of high tensile strength appears desirable in order for it to withstand the pressure developed within the extruded portion by transmission of the extrusion pressure down through the ceramic core which may act essentially as a fluid under extrusion conditions.

#### Future Work

1. Aluminum coextrusion can having a wall thickness

of approximately  $3/8$ " rather than  $1/8$ " are being made to see if the increased wall thickness will effectively combat the bursting which occurred in the present work.

2. A number of Monel metal extrusion blanks and coextrusion cans are being made for use in the extrusion of barium titanate. The solid blanks of the Monel metal will be used first to check the extrusion characteristics of the metal itself prior to attempting coextrusion with the barium titanate.

3. More 1018 carbon steel cans will be made for use in the extrusion of barium titanate.

Progress Report - Part V

LOW LOSS MICROWAVE CERAMIC DIELECTRICS

Introduction

The solution of this problem is to develop low loss insulation with a dielectric constant of 15 and a power factor not to exceed 0.004 at microwave frequencies and at temperature between -50 and +300°F. The dielectric constant is above that of the recognized range for insulation.

In earlier work dielectric properties were measured and reported for various compositions. The main problem in preparing these compositions by either hot-pressing or solid-state reactions was that they had a short firing range. This problem had to be alleviated before reproducible results could be obtained.

In an attempt to increase the firing range, the composition was pre-reacted. The material was fired to a temperature where it was fluid and then quenched in water. The quenched material was analysed for compounds, crushed, screened and then pressed into discs and fired.

Procedure

The compositional body K15+2 was prepared in the way explained in earlier reports. The prepared material was placed in a platinum crucible with a cover and heated in an induction furnace.

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### Results

The composition started to become fluid at 1570°C. After soaking the melt for 15 minutes the entire crucible was placed into a pan of water. X-ray analysis revealed that the melt was mostly glass with only cristobalite remaining in the crystalline form. The material was then crushed in a mortar and pestle and passed through a 100 mesh screen. Discs were prepared in 3/8" dies and then were fired to various temperatures using draw trails in an electric furnace. The dielectric properties at 1 megacycle and various firing temperatures are listed below.

<u>Tem. °f</u>	<u>K</u>	<u>Tan δ</u>
2180	12.35	.00130
2200	11.60	.00147
2210	12.00	.00192
2220	11.65	.00186
2240	13.00	.00130
2280	11.70	.00133
2310	11.36	.00148
2320	11.70	.00276
2350	11.60	.00178

The best firing temperature was at 2240°F. The material prepared in this way had a very long firing range. The discs were X-rayed and a polished section was made. The results indicated that  $\text{La}_2\text{O}_3$ ,  $1\text{La}_2\text{O}_3 \cdot 2\text{SiO}_2$ ;  $\text{La}_2\text{O}_3\text{-SiO}_2$

and cristobalite were present but that a large percentage of glass remained in the discs.

Since the discs were drawn out of the furnace and not allowed to cool slowly, the amount of glass in the discs would probably remain high. Furthermore a lower  $\tan \delta$  and a higher dielectric constant was obtained for the same composition by the hot-pressing technique previously reported. Thus, the conclusion that was drawn from these two conditions was that the discs contained a large amount of glass. The discs were subsequently heat-treated for several hours at various temperatures in an electric kiln. The object of this process was to devitrify some of the glass and to start crystal growth. The results of this approach are given below.

After-fire Heat Treatment				
<u>Fire °F</u>	<u>Temp. °F</u>	<u>Soak</u>	<u>K</u>	<u>Tan <math>\delta</math></u>
2220		None	11.65	.00186
	1900	4 hours	10.5	.00131
	2000	6 hours	9.9	.00150
2210		None	12.0	.00192
	2100	6 hours	11.9	.00073
	2140	6 hours	11.9	.00072
	2200	2 1/2 hrs.	11.7	.00101
2200		None	11.60	.00147
	2140	6 hours	11.70	.00056
	2200	2 1/2 hrs.	11.78	.00090

The dielectric constant of the discs fired at 2200°F was appreciably reduced with the two subsequent firings;

however, the power factor changed only slightly. X-ray analysis revealed that there was an increase in the amount of crystalline material after 2000°F fire than after the first fire. With the discs fired at 2210 and 2200°F, a heat-treatment to 2140°F produced the lowest power factor.

When both of these discs were fired to 2200°F the power factors went up markedly. These discs started to slump which indicated that the amount of glass was increasing. The improvement in power factor is undoubtedly due to continued crystal formation or growth resulting in tying the more lossy ions in the crystalline phase where they contribute much less to lossiness. When the power factor starts to increase again the crystals are being dissolved resulting in a higher glass content which increases the power factor.

Thus, the process of prereacting the compositions by attempting to frit results in carrying the reactions to a much greater degree of completion. This in turn results in the bodies, prepared from the powdered prereacted composition, having a lower maturing temperature and a long firing range. With an after-fire heat treatment of the proper magnitude, the power factor is reduced from .0018 to .0005 when measured at 1Mc.

#### New Compositions

Besides the work on the lanthanum-alumina-silicates other compositions are being studied which show promise of



meeting the technical requirements. Such a system which has favorable dielectric properties at 1Mc is the magnesia-zirconia-titania system.\* Microwave frequencies were not evaluated for this system. The two most favorable compositions in this system have the mole ratios of 2:1:2 and 4:1:4. The table below gives the compositions, dielectric properties and firing temperature.

<u>Mole Ratio</u>	<u>Weight %</u>			<u>1Mc</u>		
	<u>MgO</u>	<u>2.Oz</u>	<u>tiOz</u>	<u>temp°C</u>	<u>K</u>	<u>Tan δ</u>
2:1:2	22.0	34.0	44.0	1550	18	.033%
4:1:4	26.8	20.4	52.8	1500	18	.020%

One hundred gram batches were weighed out. The batches were ball milled in the dry state. Discs prepared from this material were fired on platinum foil and calcined for 4 hours at 2000°F. The samples were then pulverized with a mullite mortar and pestle.

Discs made from material with the 4:1:4 and 2:1:2 mole ratios were fired in a mullite tube placed in an electric furnace. The tube was necessary since an oxygen atmosphere was applied in the second firing. This atmosphere was necessary so that the material would not reduce. The results of this firing at 1Mc are recorded below.

<u>Mole Ratio</u>	<u>Firing Temp. °C</u>	<u>Soak</u>	<u>K</u>	<u>Tan δ</u>
2:1:2	1550	1 hour	20.4	.0010
4:1:4	1500	2 hours	19.9	.0009

The two compositions prepared appeared to be slightly immature. This could account for the slight difference between our measured data and the published data on these compositions. The results are extremely promising and will be evaluated at microwave frequencies.

#### Summary

Considerable difficulty has been encountered in the preparation of the lanthanum oxide, alumina-silica type compositions. The evaluation of the material with the new procedure has resulted in ceramic bodies of low maturing temperature and a longer firing range. This procedure entails melting or near-melting of the complete composition, quenching to attain a complete glass or to retain the maximum glass content, pulverizing the glass, preparing specimens and then firing the specimens. After the specimens were fired and measured, it was realized that they contained too much glass. The next step in the procedure was to subject the samples to an after-fire heat treatment in an attempt to devitrify some of the glass.

The results utilizing the devitrification technique indicated that the amounts of glass in the specimens can be varied by the after-fire heat treatment and that this

change together with crystal growth had a great effect on the power factor changing it from .0014 to 0.0005. In future work this technique will be used and the amount of glass will be measured. Although the electrical measurements were not made at ultra-high frequencies, the results obtained did indicate that this type composition and procedure is extremely promising.

With the magnesia-zirconia-titania systems, low loss specimens have been prepared with a dielectric constant at approximately 19 at 1Mc. This system will be analyzed carefully to lower the dielectric constant to between 12 and 15 and prepare specimens for evaluation at microwave frequencies.

#### High Frequency Properties of a Lanthanum Aluminosilicate Composition

In the last report several lanthanum aluminosilicate compositions (K15+1 and K15+3) were hot pressed and evaluated in the microwave frequency range.  $\tan \delta$  could not be determined with any degree of accuracy as the samples were not long enough. One composition K15+2 whose composition is  $\text{La}_2\text{O}_3 60.99$ ,  $\text{Al}_2\text{O}_3 6.22$  and  $\text{SiO}_2 32.81$  had been prepared but not fabricated. It has since been fabricated and evaluated at 9.4 KMc and at 30 and 300°C. Two sample lengths were evaluated to arrive at the correct dielectric constant. The results are as follows:

<u>Temperature</u>	<u>Sample Length</u>	<u>Dielectric Constants</u>	<u>Tan <math>\delta</math></u>
30°C	1	7.6, 15.5, 20.5	.000042
	2	5.3, 12.4, 20.0	-----
300°C	1	20.5	.000012

In the past, the last report in particular, it had been assumed the dielectric constant was approximately 15 from 1 Mc. data. It is now obvious that it is approximately 20. The earlier data must be re-evaluated.

From the data above the dielectric constant is 20.5 over the temperature range 30 to 300°C, and the tan  $\delta$  is extremely low, lower than .00005. This dielectric constant is above the 12-15 range required for this problem and can be lowered into the range. The Tan  $\delta$  is well below the requirements of the problem.

#### Future Work

1.  $\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$  will be prepared by: a) Hot pressing, b) Quenching and c) by solid phase reaction; and ultra-high frequency measurements made.

2. Ultra-high frequency measurements of the magnesia-zirconia-titania system.

3. Investigations of the calcium stannate type composition which appears promising for the technical requirements of this report.

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Koenig, E. J. Smoke, C. J. Phillips, et al.  
SIGNAL CORPS REPORT NO. II, February 1 to  
May 1, 1962. Contract DA-36-039-sc-891411

Unclassified report

Under Devitrified Ferroelectrics, bodies were made from the C.P. barium titanate glass and fired to vitrification. The Curie temperature is 141°C, and as high as 155°C depending on thermal history. Under certain conditions the dielectric constant is higher above the Curie temperature than below. The crystal size resulting from devitrifying the glass in the range of 0.5 to 2μ. Under Low Loss Boron Nitride Dielectric a study of the deterioration of several electrical properties of the hot pressed material indicates that it is due to a surface phenomenon and relative humidity above 50% results in rapid degradation.

( over )

Similar results are obtained with a sintered specimen. Under Structural Studies of Polycrystalline Ceramics a procedure has been devised to fire on Moly-manganese metallizing and thermal condition in the same firing. Under Hot Extrusion, the capability of the equipment was demonstrated by the extrusion of a solid slug of aluminum metal and the coextrusion of aluminum clad, glass bonded mica, however the quality was not satisfactory. An experiment showing the flow pattern during extrusion is described. Under Low Loss Micro-wave Dielectrics, difficulties have been encountered in making and reproducing the tantanum alumina-silicate type composition. An attempt at pre-reacting the ingredients by fritting resulted in a lowered firing temperature and long firing range. An after fire heat treatment lowered the power factor to 0.0004 at 1Mc.

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